

**METHOD FOR PREPARING EFFICIENT LOW VOLTAGE PHOSPHORS
AND PRODUCTS PRODUCED THEREBY**

Background of the Invention

1. Field of the Invention

The present invention generally relates to methods for preparing cathodoluminescent phosphors using a sol-gel condensation technique, as well as to products made from these methods. In particular, the present invention relates to methods for preparing cathodoluminescent phosphors (e.g., orthosilicate-based phosphors) exhibiting superior brightness and efficiency, making them especially suitable for low voltage operation in various applications such as flat panel displays, field emitter displays (FEDs), electroluminescent displays (ELDs), TVs, and the like.

2. Description of the Background Art

Phosphors in general comprise a wide band gap semiconductor matrix with homogeneously dispersed activator ions within. Currently accepted mechanisms of light output in cathodoluminescence phosphors, though not well understood, include electron-induced creation of excitons, which can result in photon emission through recombination of the holes and electrons. However, lattice defects, impurities, charge traps, etc. can impede the efficient recombination of these charge carriers,

1 thus causing the nonradiative decay of the excited states. It is believed that the
2 phosphor crystal structure should be as close to perfect as possible to achieve
3 efficient emission of light.

4 Current commercially-available cathodoluminescent phosphors are made for
5 high voltage (i.e., approximately 5-20 kV) applications. On information and belief,
6 bright and efficient phosphors that are especially suited for low voltage operation
7 (at or below about 1-6 kV, preferably 2-3 kV) do not exist in the prior art. Thus, it
8 would be very desirable to provide cathodoluminescent phosphors having superior
9 brightness and efficiency at low voltages (e.g., below about 2000 volts) for field
10 emitter displays mainly due to the requirement of the very close proximity of the
11 phosphor screen to the electron source (i.e., the field emitter arrays). Low bias
12 voltages reduce the serious problems of electrical insulation breakdown and arcing.

13 Many conventional cathodoluminescent phosphors, such as those based on
14 orthosilicates with grain sizes of a few micrometers, are prepared by mixing
15 micron-sized or larger precursor particles and firing at high temperatures to induce
16 solid reactions. For example, to make green Mn-doped zinc-orthosilicate phosphors,
17 particles of Mn-doped zinc oxide (ZnO) are mixed with SiO₂ particles and fired at
18 high temperatures to produce the phosphor compound Zn₂SiO₄:Mn via solid
19 reaction. The objective of this conventional method would be to cause homogeneous
20 fusion of the precursor components, uniform incorporation of the activator (or

1 dopant) species, and good crystal structure formation. However, due to the
2 slowness of solid fusion/reactions, especially between large particles, good
3 homogeneity is not easily achieved. Lattice defects and even non-stoichiometrical
4 components can result, leading to poor semiconductor electronic band structures,
5 including gap states that can easily cause nonradiative decay. Furthermore,
6 portions that have an activator (e.g., Mn) deficiency can be formed, contributing to a
7 "dead layer" that gives no light output. Other portions can potentially have excess
8 amounts of the activator species which can quench each other, resulting in
9 decreased light output.

10 U.S. Patent No. 5,985,176 to Rao discloses Mn^{2+} -activated zinc orthosilicate
11 phosphors having the empirical formula:



12
13 wherein $0.005 < x < 0.15$. The phosphors described in this patent are said to exhibit
14 the properties of "improved brightness and decreased persistence" (column 3, lines
15 3-12) and are made by using the sol-gel process (column 3, lines 13-24 and column
16 5, line 7 to column 6, line 11). According to the patent, a high degree of
17 homogeneity is achievable because the starting materials are mixed at the
18 molecular level in a solution (column 3, lines 27-29). Unlike the present invention,
19 however, this patent discloses the use of tetraethoxysilane (TEOS) instead of a solid
20 precursor.

1 Commonly-owned, copending U.S. Application No. 09/398,947, filed on
2 August 2, 1998, which is incorporated herein by reference for all purposes, discloses
3 phosphor nanoscale powder prepared by forming a solution or slurry comprising
4 phosphor precursors and then firing the solid residue of the solution or slurry. In
5 Example I of the '947 application, a mixture of Zn and Mn(II) or Cu(II) precursors
6 (e.g., zinc and manganese(II) acetates) is refluxed in ethanol to obtain a mixed
7 solution of alkoxides/acetates of 1 wt.% Zn, with the amount of Mn being in the
8 range of 1-4% with respect to the weight of Zn. The mixed alkoxide/acetate is then
9 cooled and hydrolyzed with tetramethylammonium hydroxide to form a sol
10 comprising of a suspension of mixed nanoparticles of metal oxides. After that,
11 AEROSIL® fumed silica (7 nm in diameter, Degussa Corporation) is introduced into
12 the sol to form a suspension of the particle precursors. Following ultrasonication,
13 cooling, and drying, the resulting mixed gel is then pre-fired, cooled, ground, and
14 fired. In contrast, in a typical embodiment of the present invention, a Zn-Mn
15 alkoxide solution is first prepared from Zn and Mn alkoxide precursors without
16 hydrolysis or forming particles. In fact, an inhibitor such as nitric acid is typically
17 added to prevent premature (i.e., before introduction of the second precursor
18 particles) precipitation of particles. The second precursor particles (e.g., fumed
19 silica) are then added to the solution of the Zn-Mn alkoxide mixture, followed by
20 induced precipitation of the first precursor by sol-gel condensation reaction, the

Summary of the Invention

It is yet another object of the present invention to provide a method for preparing phosphors (e.g., orthosilicate phosphors) exhibiting continued higher brightness and/or luminous efficiency with increasing voltage.

1 It is a further object of the present invention to provide a method for
2 preparing phosphors (e.g., orthosilicate phosphors), wherein the method provides
3 more favorable conditions (e.g., shorter firing duration) for the homogenous fusion
4 of the precursors than that used in the manufacture of commercial orthosilicate-
5 based phosphors.

6 These and other objects of the present invention are achieved by adding solid
7 particle precursors to an activator ion-doped alkoxide solution, inducing a sol-gel
8 condensation, drying the mixture, and then calcinating (or firing) the resulting
9 mixture. Thus, in one aspect, the present invention provides a method for
10 preparing phosphors comprising the steps of:

- 11 (a) providing a solution comprising an alkoxide precursor and a dopant
12 precursor;
13 (b) mixing said solution with a solid particle precursor;
14 (c) inducing a sol-gel condensation reaction to form a sol-gel condensation
15 reaction mixture;
16 (d) drying the sol-gel condensation reaction mixture; and
17 (e) firing the dried reaction mixture at a temperature sufficient to form
18 phosphors.

19 In other aspects, phosphor products made in accordance with the present
20 invention are also contemplated.

Brief Description of the Drawings

Figure 1 compares the brightness (cd/m^2) of the $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphor of inventive Example 1 against a commercial $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphor (RCA P1) at various beam voltages.

Figure 2 compares the luminous efficiency (lm/W) of the $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphor of inventive Example 1 against a commercial $\text{Zn}_2\text{SiO}_4\text{:Mn}$ phosphor (RCA P1) at various beam voltages.

Description of the Preferred Embodiments

It has been discovered that, in comparison to conventional or commercial phosphor production technology, the present invention achieves a different and a more favorable condition for the homogeneous fusion of the precursors. In this invention, solid particle precursors (e.g., SiO_2 nanocrystals) are initially mixed with a solution of an alkoxide precursor (e.g., zinc alkoxide) and a dopant precursor (e.g., manganese alkoxide), at suitable concentrations and proportions, before solid oxide (e.g., ZnO and MnO) particles form. A sol-gel hydrolysis-condensation reaction is then induced in the presence of the solid particle precursor so as to permit the formation of a coating of a doped alkoxide gel polymer around each solid particle precursor. It should be noted that the coating may, but not necessarily, have non-uniform thickness around the solid particle. In the drying and firing process, an

1 oxide shell, in complete contact with the solid particle precursor, is formed. Thus,
2 the contact area is much larger than in the case when the synthesis involves mixing
3 of solid precursor particles. In particular, a lower temperature, a much shorter
4 solid reaction time as well as superior homogeneity can be expected.

5 In the present invention, a solution containing at least an alkoxide precursor
6 and a dopant precursor is first provided. Typically, but not necessarily, the solution
also comprises a hydrolysis agent and/or a reagent capable of inhibiting premature
condensation reaction in the solution prior to the addition of the solid particle
precursor.

10 The alkoxide precursor can be any alkoxide that can form a phosphor and is
11 suitably a metal alkoxide. Such metal alkoxide precursors include, but are not
12 limited to zinc alkoxides. When zinc alkoxide(s) are selected, they may be selected
13 from zinc methoxide, zinc ethoxide, zinc propoxide, zinc butoxide, and others.

14 There is also no limitation with respect to the dopant precursor, so long as a
15 phosphor can be produced. Typically, the dopant is selected from an acetate, an
16 alkoxide, an organometallic compound, or an inorganic salt of the metal (dopant
17 ion), and mixtures thereof. Good results have been obtained using metal alkoxides
18 such as manganese methoxide, as well as acetates such as europium acetate;
19 successful results would also be expected for other dopant precursor species such as
20 manganese nitrate.

1 The solvent is any liquid that can provide a solution of the above-described
2 alkoxide precursor, dopant precursor, and other optional reagents without
3 interfering with the subsequent sol-gel reactions. Usually, the solvent is an organic
4 solvent such as 2-methoxyethanol or ethanol.

5 If present in the initial solution, the hydrolysis agent can be selected from
6 various compounds such as water, tetramethylammonium hydroxide or mixtures
7 thereof.

8 Additionally, a reagent capable of preventing premature hydrolysis and/or
9 condensation reactions in the initial solution is desirably present. If present, it may
10 be selected from various compounds such as nitric acid, hydrochloric acid, and
11 mixtures thereof.

12 The order of adding the components of the solution is also not limited.
13 Typically, the alkoxide precursor and the dopant precursor are dissolved in the
14 solvent and refluxed for an appropriate time. Then, additional solvent, hydrolysis
15 agent and/or a reagent capable of preventing hydrolysis may be added continuously
16 or incrementally. The resulting solution is usually transparent and remains stable
17 for an extended period of time (e.g., 30 days).

18 The amount of the various components in the solution is not particularly
19 limited and can be determined on a case-by-case basis by one skilled in the art.
20 Typically, the amounts of the alkoxide precursor and the dopant precursor are such

1 that the molar ratio of the dopant precursor to the alkoxide precursor is from about
2 1/100 to about 5/100. The amount of solvent can range from about 1,000 to about
3 100,000 ml per mole of alkoxide precursor. Further, the amount of the hydrolysis
4 agent may range from about 0 to about 10 moles per mole of alkoxide precursor and
5 depends on the number of alkoxide groups per precursor molecule, while the
6 amount of the reagent capable of preventing premature hydrolysis and/or
7 condensation (i.e., prior to step (b) in the method above) in the solution may range
8 from about 0 to about 1 mole per mole of alkoxide precursor. There is an optimal
9 dopant to host metal ratio, usually determined empirically as a tradeoff between
10 having enough dopants for light output and not having enough dopant that they
11 quench themselves through non-radiative channels. Too much hydrolysis agent
12 may induce premature or immediate sol-gel condensation reaction, while too much
13 condensation inhibitor may prevent the condensation reaction altogether.

Ins. A3 14 > ~~After the solution containing at least the alkoxide precursor and the dopant~~
15 precursor is provided, a solid particle precursor is then added. Typically, the solid
16 particle precursor is nanoparticulate, although particles in the micron range may be
17 used. By the term "nanoparticulate" and "nanoparticles," it is meant that the
18 particles have a greatest dimension of about 100 nm or less, and should be as small
19 in size as possible, preferably less than 10 nm. Typically, these nanoparticles may
20 be ~~silica, metal oxide, metal sulfide, metal oxysulfide, metal halide, metal~~

1 ~~carbonate, metal phosphate, metal sulfate, semiconductor oxide (e.g., germanium~~
2 oxide), pure metal or mixtures thereof. Specifically, silica such as fumed silica,
3 V_2O_5 , Y_2S_3 , $GdOS_2$, ZnO , GdS_3 , La_2O_3 , Al_2O_3 , CdS , and the like may be used. With
4 respect to silica, AEROSIL[®] fumed silica from Degussa Corporation can be used.
5 The amount of solid particle precursor usually is close to the stoichiometric amount
6 determined by the phosphor compound, although the proportions for optimal light
7 output are to be adjusted (or fine-tuned) empirically. Obviously, if the proportions
8 are too far off, the desired phosphor compound and crystal structure cannot be
9 ~~formed properly.~~

10 It should be noted that the mixing of the solid particle precursor and the
11 solution is preferably performed under conditions preventing any condensation
12 reactions. Preferably, the mixture is subjected to treatment such as ultrasonication
13 to ensure good dispersion of the solid particle precursor. If a hydrolysis agent is not
14 included in the solution of the alkoxide precursor and the dopant precursor, it may
15 be added at any point during or after the mixing of the solid particle precursor and
16 the solution. For example, the solution of the first precursor alkoxide and the
17 dopant alkoxide can be made first without the addition of H_2O (or another
18 alternative hydrolysis reagent). The solid particle precursor is then mixed with the
19 solution, followed by the addition of H_2O (or another hydrolysis reagent) with or
20 without any additional stabilization (i.e., inhibiting) reagents.

1 After the mixing of the solid particle precursor and the solution is complete, a
2 sol-gel condensation reaction is initiated. This is usually accomplished by
3 subjecting the mixture to a temperature from about 50°C to several hundred
4 degrees °C for several minutes to several hours. At this point, a polymeric alkoxide
5 gel is formed around each particle of the solid particle precursor.

6 It should be understood here that additional or optional components and/or
7 ingredients may be added at an appropriate point in the process of the present
8 invention. For example, it may be desirable to incorporate an alcohol, such as
9 ethanol, in the mixture (after the sol-gel condensation has taken place) of the
10 present invention to promote drying and spreadability of the mixture on a
11 substrate. If used, the optional alcohol may be present in an amount of from about
12 1,000 to about 10,000 ml/mole of alkoxide precursor. If too much optional alcohol is
13 used, not enough material may be transferred or processed per layer.

14 The mixture containing the polymeric alkoxide gel is then subject to drying
15 and firing to form the phosphors of the present invention. In one embodiment, the
16 mixture containing the gel is first spread uniformly over a substrate (e.g., a metal
17 plate, quartz plate, or the unpolished side of a silicon wafer) to form a film.
18 Conventional techniques such as dipping, spin-coating, and other methods may be
19 used to apply the gel on the substrate. After the layer is applied, the film is dried at
20 about 100 to about 300 °C for a few minutes, either continuously under the same

1 conditions or stepwise under different conditions. More than one layer may be
2 deposited on the substrate.

3 The film is then fired at about 800 to about 1,400 °C, depending on the
4 phosphor compound, for about 0.25 to about 1 hour to obtain the final phosphor
5 product. The temperature will depend on the nature of the solid precursors and is
6 determined by their fusion and solid state reactions.

As would be apparent to one skilled in the art, the present invention is not
restricted to the formation of thick films as described in the embodiments earlier.
Instead of drying the precursor mixture on a substrate, the mixture of the solid
particle precursor (e.g., silica nanopowder) and the doped-alkoxide solution, first
mixed at room temperature prior to sol-gel condensation reactions, can simply be
heated to some elevated temperature such as 150°C in a crucible to evaporate the
solvent and complete the sol-gel condensation reaction, followed by similar
procedures of heating and calcination in oxygen. The resulting solid can be ground
and be used directly as a phosphor powder.

The same approach used in this invention can be applied to the preparation
of any phosphor for which one of the precursors, excluding the dopant precursor, is
in solid particle (typically nanoparticle) form and the other precursors exist in or
can be converted to alkoxides in solution form. The important factor is to mix the
precursors before any precipitation or condensation has occurred in the alkoxide

1 solution. Blue, green, and red phosphors are contemplated herein. Blue phosphors
2 include, but are not limited to, $\text{Y}_2\text{SiO}_5\text{:Ce}$, which can be made from yttrium
3 alkoxide, cerium alkoxide, and SiO_2 . Green phosphors include, but are not limited
4 to, $\text{ZnSiO}_4\text{:Mn}$, which can be made from zinc alkoxide, manganese alkoxide, and
5 SiO_2 . Red phosphors include, but are not limited to $\text{Y}_2\text{O}_2\text{S:Eu}$, which can be made
6 from yttrium alkoxide, europium acetate, and Y_2S_3 . Of course, other species are also
contemplated. For a $\text{YVO}_4\text{:Eu}$ phosphor, a Y-Eu alkoxide solution is first made and
stabilized against premature condensation. Then V_2O_5 nanoparticles are mixed
with the Y-Eu alkoxide solution. Sol-gel condensation is then induced, followed by
the drying and calcination at suitable temperatures.

As described previously, the solid particle precursor can be larger than 0.1
micron size (exceeding the nanometer size regime). Advantage can still be gained
by the intimate contact between the particle and the shell of other oxides
surrounding it before calcination.

Additionally, instead of using distinct particle precursors, aerogel precursors
which comprise high porosity structures made of interconnected nanoparticles can
be used. The high porosity, up to 99%, provides the extremely high surface/volume
ratio required for high surface contact between the solid precursor and the
surrounding oxide shell.

EXAMPLES

The following examples illustrate certain embodiments of the present invention. However, they are not to be construed to limit the scope of the present invention in any way.

Example 1

(A) Preparation of Mixed Zn-Mn Alkoxide Solution:

A mixture of 1.0136 g of zinc butoxide and 0.0101 g of manganese methoxide at a molar ratio of Mn/Zn=0.018 was dissolved in 10.0 ml of 2-methoxyethanol and refluxed for 1 hour at 80 °C, under nitrogen flow, to give a clear, light brown 0.48M (Zn) solution (stock). A mixture of 19.0 ml of 2-methoxyethanol, 0.15 ml of water and 0.02 ml of nitric acid (the latter being a reagent for inhibiting premature hydrolysis and condensation) was added to 5.0 ml of the stock solution to give a final 0.1M (Zn) solution. The solution remained transparent with no precipitation. The solution remained clear and stable for many weeks.

(B) Introduction of the Silica Nanoparticles:

0.010 g of AEROSIL® 150 (SiO₂, 7 nm diameter, Degussa Corporation) was introduced into 3.70 ml of the above 0.1M alkoxide solution (in a proportion

1 with a molar ratio of Si/Zn=0.45) at room temperature and ultrasonicated for
2 dispersion of the AEROSIL® 150 particles. At this point no condensation reaction
3 had taken place, as evidenced by the settling of the AEROSIL® 150 particles over a
4 relatively short time and the solution above them remained clear.

5
6 (C) Initiation of Sol-Gel Condensation Reactions:

The mixture in (B) was heated to and maintained at 80°C while being
agitated. In about 90 minutes the solution became homogeneous and translucent.

10 (D) Preparation of Mixed Thick Film:

- 11 (1) A fixed small quantity of the mixture in (C) was spread as
12 uniformly as possible over the back unpolished side of a 1 x 1 cm
13 piece of silicon wafer at room temperature and then dried at
14 100°C for 5 minutes, followed by further drying at 200°C for 5
15 minutes in room atmosphere.
- 16 (2) A second layer of the material was added on top of the layer in
17 (1) using the same dispensing and drying procedure. It should
18 be noted at this point that as many layers as desired could be
19 added. In this example, a 40 layer thick film was built up using
20 the same procedure.

1 (3) The thick film in (2) was heated in a quartz tube oven under
2 flowing oxygen for 30 minutes at 350°C. The temperature was
3 then increased to 1050°C over 1.5 hours and maintained at this
4 temperature for 15 minutes. The oven was then turned off to
5 allow a slow cooling down to room temperature.

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Example 2

(A) Preparation of the Mixed Zn-Mn alkoxide Solution:

The same solution as in Example 1 (A) was used

(B) Introduction of the Silica Nanoparticles:

The same procedure used in Example 1 (B) was used except that the
Si/Zn molar ratio was 0.5.

(C) No Initial Heating:

The mixture in (B) was kept at room temperature. The solution,
except for the silica powder, remained clear.

(D) Preparation of Thick Mixed Film:

(1) The mixture in (C) was shaken to ensure uniform dispersion of

1 the silica powder before dispensing in the same manner as in
2 Example 1 (D) (1), except drying was performed at about 100°C.

3 (2) A thick film consisting of 6 layers was made by repeating (1) six
4 times.

5 (3) The thick film in (2) was heated in a quartz tube oven under
6 flowing oxygen at 875°C for 30 minutes. It was then cooled
slowly to room temperature.

Example 3

10 An eight-layer thick film on a Pt film-coated silicon substrate (polished side)
11 was made using otherwise the same procedures and conditions as in Example 2.

Cathodoluminescence Measurements:

14 Cathodoluminescence (CL) properties of the thick films made in Examples 1
15 through 3 were observed, and the CL for the thick film made in Example 1 was
16 measured at an electron beam voltage of 320-3120 volts using a Minolta CS-1000
17 spectroradiometer and processed with ND filter compensation and wavelength
18 calibration. The chromaticity parameter (CIE 1931) were measured to be $x=0.2065$,
19 $y = 0.7122$. The brightness and the luminous efficiency are plotted in Figures 1 and
20 2, respectively.

1 In comparative studies, to account for possible differences due to substrates
2 and other factors, a powder film of the commercial $\text{Zn}_2\text{SiO}_4\text{:Mn}$ (RCA P1 phosphor
3 from Sarnoff Corporation) was placed on the same type of silicon substrate. The
4 thickness of the commercial phosphor film was intentionally made to be much
5 thicker than the thick film in Example 1 above. In this regard, it is known that the
6 film should be sufficiently thick so that none of the inducing electrons travel
7 through the film without colliding with the phosphors, although it is also known
8 that there would be no difference beyond a certain thickness. The two substrates
9 were adhered side by side using a conductive glue on a chrome-coated glass plate
10 mounted on a translation stage in the vacuum system. The cathodoluminescence
11 was measured on the thick film, followed by a translation to the commercial film,
12 and subsequent CL measurement without changing any electron beam parameters.
13 Then the electron beam voltage was adjusted to additional values and the same
14 comparative CL measurements were taken. No charging problem in either film was
15 observed even at the lowest beam voltage used.

16 Although CL measurements for the phosphors of Examples 2 and 3 were not
17 undertaken, these phosphors visibly exhibited a distinct luminescence similar to
18 that of Example 1.

19 As shown in Figures 1 and 2, the present invention represents a new and
20 improved method for manufacturing orthosilicate-based phosphors having high

1 cathodoluminescence, i.e., brightness and luminous efficiency, at low electron beam
2 voltages. For example, the thick film made in Example 1, far from being optimized,
3 has already outperformed the commercial phosphor at all voltages up to the highest
4 (3120V) studied. Especially significant for the phosphors of the present invention
5 are the much higher luminous efficiencies at the low voltages and the continued
6 linear rise in brightness with increasing voltage. By contrast, the brightness and
7 the luminous efficiency of the commercial RCA P1 phosphor begins to level off.
8 Specifically, at 320 volts, the luminous efficiency is 3.45 lm/watt for the thick film
9 of the present invention, whereas it is only 0.73 lm/watt for the RCA P1 powder
10 film. At 520 volts, the corresponding efficiencies are 4.54 lm/watt and 2.94 lm/watt
11 for the inventive thick film and the RCA P1 powder film, respectively. For most
12 commercial phosphors, the brightness and luminous efficiency tend to level off at
13 higher voltages. On the other hand, in the present invention, the brightness
14 continues to increase linearly and the efficiency levels off much more slowly at the
15 higher voltages.